Report No. BMI-1426

UC-25 Metallurgy and Ceramics
(TID-4500, 15th Ed.)

Contract No. W-7405-eng-92

THE DIFFUSION OF HYDROGEN IN ZIRCONIUM HYDRIDE

by

William M. Albrecht
W. Douglas Goode, Jr.

March 3, 1960

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
THEORETICAL CONSIDERATIONS	1
EXPERIMENTAL WORK	4
Materials	4
Method	4
RESULTS AND DISCUSSION	6
SUMMARY	9
REFERENCES	9

THE DIFFUSION OF HYDROGEN IN ZIRCONIUM HYDRIDE

William M. Albrecht and W. Douglas Goode, Jr.

The diffusion of hydrogen in zirconium hydride was studied using permeation techniques. The rate of permeation of hydrogen through zirconium hydride disks was measured for small concentration gradients. Data were obtained at 61 to 65 a/o hydrogen and 500 to 750 C. The diffusion coefficients were determined by the time-lag method. No variation of the diffusion coefficients with hydrogen concentration was observed. The diffusion coefficients can be expressed by

$$D \text{ (cm}^2 \text{ per sec)} = 599 \exp (-34,800/RT).$$

INTRODUCTION

A study of the diffusion of hydrogen in beta zirconium (9 to 33 a/o hydrogen) has been reported in BMI-1373(1). It was the purpose of the present study to determine the diffusion coefficients of hydrogen in zirconium hydride having compositions of 61 to 65 a/o hydrogen.

THEORETICAL CONSIDERATIONS

The diffusion coefficient for a gas in a metal can be determined from permeation measurements in the following manner. Consider a metal barrier of thickness, ℓ , having a uniform concentration, C_2 , of the permeating gas. The original pressure of the gas on both faces of the barrier is the equilibrium pressure associated with the concentration, C_2 , at the temperature of the experiment. Permeation is initiated by increasing the pressure on one side of the barrier to the equilibrium pressure associated with a concentration, C_1 . First, consider that the concentrations, C_1 and C_2 , are maintained constant throughout the experiment. These conditions may be described by

$$C = C_1 \text{ at } x = \ell \text{ for all } t,$$

$$C = C_2 \text{ at } x = 0 \text{ for all } t,$$

$$C = C_2 \text{ at } t = 0 \text{ for } 0 < x < \ell,$$

where

C = concentration of the gas in the metal per unit area perpendicular to the direction of mass flow through the metal

(1) References at end.

x = distance along the direction of mass flow in the metal from the downstream face of the barrier

t = time, measured from the initiation of permeation.

The solution of Fick's second law of diffusion⁽²⁾ for these boundary conditions is given by Crank⁽³⁾. The equation for the amount of gas permeating the disk is

$$Q_t = (C_1 - C_2) \frac{Dt}{\ell} + \frac{2\ell}{\pi^2} \sum_{n=1}^{\infty} \frac{C_1 \cos n\pi - C_2}{n^2} \left\{ 1 - \exp \left[-Dn^2\pi^2 t / \ell^2 \right] \right\} \\ + \frac{4C_2\ell}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \left\{ 1 - \exp \left[-D(2m+1)^2\pi^2 t / \ell^2 \right] \right\}, \quad (1)$$

where

Q_t = the quantity of gas that has permeated the disk in time, t

D = the diffusion coefficient.

Equation (1) is shown in Figure 1, in which Q_t in milliliters STP of gas is plotted against time in seconds using assumed values of $(C_1 - C_2)$ and D . It is seen that the curve approaches a straight line which is indicated by the dotted line in Figure 1. The equation for the straight line obtained by solving Equation (1) for $t \rightarrow \infty$ is

$$Q_t = (C_1 - C_2) \frac{Dt}{\ell} - (C_1 - C_2) \frac{\ell}{6}. \quad (2)$$

Integrating Equation (2) and multiplying by the surface area of one face of the disk, A , yields

$$F = dQ_t/dt = (C_1 - C_2) DA/\ell, \quad (3)$$

where F is the "steady-state" rate of permeation. Thus, when the equilibrium concentrations, C_1 and C_2 , associated respectively with the gas pressures, p_1 and p_2 , on both sides of the disk are known, the diffusion coefficient may be determined from the experimental steady-state rate of permeation.

A second method for determining the diffusion coefficient⁽⁴⁾ is derived from the value of the intercept, L , on the time axis of the line formulated in Equation (2). (See the broken line in Figure 1.) This value, L , is called the time lag and is associated with the time required to attain steady-state conditions in the disk. It is seen that when $Q_t = 0$ in Equation (2) that

$$L = \ell^2/6D. \quad (4)$$

The time-lag method has the advantage of being independent of concentration. Barrer⁽⁵⁾ has discussed the possibility that the effective surface concentration during permeation may not be that determined by equilibria studies.

A - 33184

FIGURE 1. THEORETICAL CURVE FOR PERMEATION

Now, consider the case in which the concentration, C_1 , is maintained throughout the experiment, but the gas permeating the disk is allowed to collect in a volume on the downstream side of the disk. Thus, the pressure, p_2 , and consequently the concentration, C_2 , on the downstream side of the disk would increase with time. The analysis of the diffusion process may be simplified by allowing the increase in C_2 to be small with respect to the difference in concentrations, $C_1 - C_2$. Thus, the rate of permeation would not be greatly affected, and the following substitutions may be made in Equation (2):

$$(C_1 - C_2) \approx (p_1 - p_2) \Delta C / \Delta p,$$

$$Q_t = (p_2 - p_a) \Delta Q_t / \Delta p_2,$$

where p_a is the original pressure at which the sample attained equilibrium ($p_a = p_2$ at $t = 0$). Equation (2) then may be written

$$\frac{p_2 - p_a}{p_1 - p_2} = \frac{\Delta C / \Delta p}{\Delta Q_t / \Delta p_2} \left(\frac{Dt}{\ell} - \frac{\ell}{6} \right). \quad (5)$$

The experimental data may then be plotted on a graph of $(p_2 - p_a)/(p_1 - p_2)$ versus time. A linear (steady-state) rate is obtained after an initial period of time. The values of $\Delta C / \Delta p$ and $\Delta Q_t / \Delta p_2$ may be determined, respectively, from equilibria data and the calibrated collection volume. The diffusion coefficient then can be calculated from the data. It is seen that when $(p_2 - p_a)/(p_1 - p_2) = 0$ in Equation (5) the formula for the time lag [Equation (4)] is obtained.

Limited equilibria data in the zirconium-hydride phases are available for use in the steady-state method. Therefore, the time-lag method was considered the better method to determine diffusion coefficients of hydrogen in zirconium hydride.

EXPERIMENTAL WORK

Materials

Arc-melted iodide zirconium rod was fabricated into sheets 0.1 to 0.15 cm thick. Disks 2.22 cm in diameter were cut from these sheets. Results of spectrographic, chemical, and vacuum-fusion analyses of the fabricated metal are given in Table 1. The metal was reacted with hydrogen to produce the hydride.

Pure hydrogen was obtained from the thermal decomposition of uranium hydride prepared from dry, tank hydrogen and degreased uranium chips.

Method

Each zirconium-disk sample was polished through 240-, 400-, and 600-grit silicon carbide paper. It was then placed in the stainless steel permeation cell which was designed so that the sample could be sealed between two compression rings 1.27 cm

TABLE 1. ANALYSIS OF IODIDE ZIRCONIUM
FOR DIFFUSION STUDIES

Element	Analysis, ppm
Iron	550
Hafnium	500
Aluminum	200
Molybdenum	200
Silicon	100
Nickel	50
Copper	50
Calcium	50
Lead	30
Chromium	30
Boron	<10
Manganese	<10
Magnesium	<10
Oxygen	330
Nitrogen	10
Hydrogen	30

(1/2 in.) in diameter by bolting the two flanged sections together. The cell was then sealed into the permeation apparatus⁽¹⁾, and evacuated below 10^{-5} mm of mercury for 16 hr. It was then heated to 800 C in a resistance furnace. The temperature of the sample was measured by a platinum-platinum -10 w/o rhodium thermocouple inserted through the downstream section of the cell so that the bead was in contact with the sample. The sample and permeation cell was degassed for at least 1 hr at this temperature.

Hydrogen was delivered to both sides of the permeation cell from the generator and storage system at the desired pressure as measured on differential oil manometers on each side of the permeation cell. Prior to initiating permeation, the sample was allowed to reach equilibrium in the hydride phase at the temperature of the experiment and the original pressure, p_a . Permeation was started by instantaneously raising the pressure on the upstream face of the disk from p_a to p_1 .

The permeation rates were determined by measuring the increase in pressure, p_2 , in the calibrated volume on the downstream side of the zirconium disk. The increase in p_2 was never greater than 10 per cent of the pressure difference across the disk. Plots of $(p_2 - p_a)/(p_1 - p_2)$ versus time were made and the diffusion coefficients obtained from substitution of the experimental values in Equation (5).

Two or three determinations of the permeation rate for hydrogen through zirconium hydride were made with each sample. Between determinations the temperature and/or pressure were set for the next run and the sample was allowed to come to equilibrium. After several days at elevated temperatures the surfaces of the disks became somewhat discolored and the disks were discarded.

RESULTS AND DISCUSSION

Diffusion coefficients for hydrogen in zirconium hydride were determined by the time-lag method in the range 500 to 750 C using samples 0.15 to 0.18 cm thick with average hydrogen concentrations of 60 to 65 a/o. The experimental pressures were chosen so that the difference in concentration between the two faces of the disk was generally less than 2 a/o. Typical permeation-rate curves obtained at 600 and 700 C are shown in Figure 2. The steady-state permeation rates and time lags are indicated.

The experimental conditions and diffusion coefficients are summarized in Table 2. The concentration level (average hydrogen concentration) was determined from equilibria data reported by Edwards et al.⁽⁶⁾ Using these data, diffusion coefficients were calculated by the steady-state method for several runs. These coefficients seemed to be in good agreement with those obtained from the time-lag data at the higher temperatures. At 600 C, there was fair agreement.

It is seen in Table 2 that the diffusion coefficients obtained at the same temperature and differing hydrogen concentrations were in good agreement. These results indicate that the diffusion rates do not vary with hydrogen concentration. The variation of the logarithms of the diffusion coefficients with reciprocal temperature is shown in Figure 3. The data can be described by the equation given on page 9.

FIGURE 2. REPRESENTATIVE PERMEATION RATE CURVES FOR HYDROGEN THROUGH ZIRCONIUM HYDRIDE

FIGURE 3. VARIATION OF DIFFUSION COEFFICIENTS WITH TEMPERATURE FOR HYDROGEN IN ZIRCONIUM HYDRIDE

TABLE 2. SUMMARY OF EXPERIMENTAL CONDITIONS AND
DIFFUSION COEFFICIENTS FOR HYDROGEN
IN ZIRCONIUM HYDRIDE

Temperature, C	Sample Thickness, cm	Pressure on Sample, mm of mercury		Average Hydrogen Concentration, a/o	Diffusion Coefficient, 10^{-7} cm^2 per sec
		P1	P2		
500	0.172	707	37.5	65(a)	1.1
600	0.175	7.2	4.1	61(a)	8.2
600	0.149	46.5	19.9	62.5	11
600	0.172	632	236	65	9.6
700	0.155	114	93.8	62.3	77
700	0.155	234	210	63.1	65
700	0.175	742	550	64.7	110
750	0.180	516	337	62.8	270
750	0.175	723	518	63.8	250

(a) Estimated concentrations. No data available in these temperature and pressure ranges.

$$D = D_0 \exp (-E/RT) . \quad (6)$$

The constants determined by the method of least squares are $D_0 = 599 \text{ cm}^2 \text{ per sec}$ and the activation energy, $E = 34.8 \pm 1.1 \text{ kcal per g-atom}$.

SUMMARY

The diffusion coefficients for hydrogen in zirconium hydride were determined from permeation studies by the time-lag method. Experiments were made at 500 to 750 C using zirconium hydride disk samples 0.15 to 0.18 cm thick having average hydrogen concentrations of 61 to 65 a/o.

Diffusion coefficients obtained at the same temperature and different hydrogen-concentration levels were found to be in good agreement. Therefore, no variation of the rate of diffusion with hydrogen concentration is indicated for the system. The diffusion coefficients can be expressed by

$$D(\text{cm}^2 \text{ per sec}) = 599 \exp (-34,800/RT) , \quad (7)$$

where 34.8 kcal per g-atom is the activation energy of diffusion.

REFERENCES

- (1) Albrecht, W. M. , and Goode, W. D. , "The Diffusion of Hydrogen in Beta Zirconium", BMI-1373 (August 25, 1959).
- (2) Fick, A. , Ann. Phys. Lpz. , 170, 59 (1855).
- (3) Crank, J. , The Mathematics of Diffusion, Oxford University Press , p 47 (1956).
- (4) Barrer, R. M. , "Stationary and Non-Stationary States of Flow of Hydrogen in Palladium and Iron", Trans. Faraday Soc. , 36, 1235 (1940).
- (5) Barrer, R. M. , Diffusion In and Through Solids, Cambridge University Press , pp 181-182 (1951).
- (6) Edwards, R. K. , Levesque, P. , and Cubicciotti, D. , "Solid-Solution Equilibria in the Zirconium-Hydrogen System", J. Am. Chem. Soc. , 77, 1307 (1955).

WMA/WDG:ayb